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VIII.—THE SAFETY OF COMMERCIAL KEROSENE OILS.

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A series of experiments were made by the writers a year ago for the purpose of determining the maximum temperature reached by the oil in the reservoirs of the most powerful modern oil lamps. A brief outline of the results of these experiments was published in the *Scientific American Supplement*, July 16, 1887. The writers found that the oil in modern lamps often reaches a temperature of 110° to 112° F., and strongly urged the use in these lamps of oil having a high flashing point, in order to avoid danger of explosion.

The legal regulations in regard to the flashing point of illuminating oils vary greatly in different parts of the country, certain States having no statutes on the subject, others requiring that no oils shall be sold which do not reach a certain standard of safety. In New York State no oil is allowed to be sold which flashes below 100° F. when tested in the manner prescribed by law, in the instrument known as the New York State Tester. Most of the prevailing legislation upon the subject is probably based upon the observations of Dr. C. F. Chandler, who sixteen years ago made a careful study of the question of the safety of burning oils.[1] Dr. Chandler found that the oil in the lamps generally in use at

[1] Am. Chemist, Aug. 1872, 43.

that time, while burning in rooms at ordinary temperature, rarely reached 100° F., but nevertheless recommended the adoption of a legal standard of flashing point not lower than 120° F. In this connection he says,[1] "The point of 100° F. does not seem high enough to secure immunity from danger, though it may be said that very few, if any, accidents occur with oil which does not flash below this temperature."

If the standard of 100° was too low to afford protection with the old-fashioned single-wick burners, it must be far more inadequate at the present day when lamps are everywhere in use which raise the oil in the reservoirs to a point fully twenty degrees higher than that reached in the lamps which Dr. Chandler tested. In modern oil lamps with double wick or circular burner, the oil while the lamp is in use is often, probably generally, heated above its flashing point. It is evident, then, that the danger of explosion is constantly present while using these lamps with ordinary oils, unless, indeed, some other cause than temperature may contribute to the safety of oils which flash above 100°. It is not proved, for example, that the vapor of such oils can, at any temperature, form violently explosive mixtures with air. So far as previous experiments have shown, kerosene explosions may be due to the presence in oils of low flashing point, of small quantities of very volatile or gaseous hydrocarbons; these constituents may be absent in oils of high flashing test, these latter may therefore not be capable of exploding. In short, no clear statement has yet been made of the relation of the flashing point of oils to their capability of giving violent explosions with air. It was in the hope of establishing such a relation, and thus determining the value of the flashing point indications as a guarantee of safety, that the experiments described in this paper were undertaken.

The questions which presented themselves for study may be briefly stated as follows:

1. Will all the hydrocarbons of which burning oils are composed, when diffused in air in proper proportions, yield distinctly explosive mixtures? If so, at what temperature for each?

2. What are the most volatile constituents of ordinary kerosene, and how do the proportions of each of these lighter hydrocarbons affect the flashing point of the oil?

It is well known that it is difficult to produce explosive mixtures

[1] Johnson's Encyc., "Petroleum," 227.

of gases at will; the experiment of exploding marsh gas with air requires very careful adjustment of proportions, or no explosion results.

A series of hydrocarbons of nearly constant boiling point was obtained by careful purification and repeated fractional distillation of lighter petroleum products. The distillation was accomplished with the aid of a long Hempel tube. In testing the possibility of producing explosions with air with the several fractions, a strong glass cylinder 30 cm. high and with a capacity of 300 cc. was employed. This was immersed nearly to its mouth in a water-bath, by means of which the experiments could be made at any desired temperature. The amount of each hydrocarbon which could be completely burned by this volume of air was calculated, and the corresponding quantity of each fraction weighed out in a thin glass bulb about ½ cm. in diameter. When a test was to be made, a little mercury was placed in the cylinder, the little bulb of hydrocarbon introduced, and the cylinder closed by a well-fitting stopper. By shaking, the bulb was then broken and its contents diffused throughout the air in the cylinder. The explosiveness of the mixture was tested by cautiously removing the stopper and applying a small flame to the mouth of the jar. The experiments were made with varying qualities of each hydrocarbon, and at different temperatures. It was found that the most violent explosions were obtained by the use of nearly the amount of the hydrocarbon which could be completely burned to water and carbon dioxide by the volume of air in the cylinder. It was shown at once, moreover, to the surprise of the experimenters, that sharp explosions could be obtained at ordinary temperatures with hydrocarbons of comparatively high boiling point, as for example with heptane, which boils at about the same point as water. The following table gives a summary of the results obtained:

Hydrocarbon.	Formula	B. P.	Source.	B. P. of Fraction.	Temperature at which explodes with air.
Butane . . .	C_4H_{10}	1° C.	C_2H_5I and Sodium.	1° C.	Ordinary.
Pentane (Iso) .	C_5H_{12}	30°	Petroleum Ether.	30°	"
Hexane . . .	C_6H_{14}	68°	" "	67–68°	"
Heptane . . .	C_7H_{16}	98.5°	"Abietene" (*Pinus Sabiniana.*)	98.5°	"
Octane . . .	C_8H_{18}	124°	Illuminating Oil.	125-130°	"
Nonane . . .	C_9H_{20}	149.5°	" "	148-150°	Between 150° and 212° F.
Decane . . .	$C_{10}H_{22}$	161° (?)		160-165°	Between 150° and 212° F.

Nonane and decane could not be made to explode with air at temperatures under 150° F., but by heating the bath to 212° F. distinct explosions were obtained. As these hydrocarbons seemed to mark the limit of the constituents of a safe oil, experiments were made under conditions similar to those which prevail in a burning lamp. A cylindrical copper vessel of about 300 cc. capacity was employed, provided with a loosely fitting cover through which a hole about $\frac{3}{16}$ inch in diameter had been bored. This was charged with a few drops of the material to be tested, and gradually heated in a water-bath, a small flame being applied to the orifice from time to time, as in the ordinary method of testing oils. The point of explosion was shown by a distinct puff which threw off the cover of the vessel. The results were more definite than those obtained by the use of the glass cylinder, and show that the legal limit as to flashing point lies between these two hydrocarbons.

Nonane exploded sharply at 79° F.
Decane " " " 104° F.

A sample of illuminating oil which showed a flashing point of 111° F. by the New York State tester gave, when tested as above, a distinct explosion at that temperature, 111° F.

The above experiments lead to the following conclusions:

1. All the paraffines up to decane, and probably also higher members of the series, may at suitable temperatures form explosive mixtures with air.

2. Oils which flash at a point considerably above the legal requirement may, under proper circumstances, give violent explosions at their flashing temperature.

3. An oil consisting of pure decane, $C_{10}H_{22}$, would be accounted a safe oil by the legal flashing point test of New York State, while one consisting of nonane would be below the standard.

In order to determine what are the lowest hydrocarbons present in ordinary burning oil, a sample of commercial "water-white" oil of excellent quality, showing a flashing point of 108° F., was carefully distilled, at first in a vacuum, and the lighter portions repeatedly fractionated by means of a Hempel tube. Two kilograms of oil yielded 30 grams of a distillate boiling at 110°–130° C., which on further rectification proved to be chiefly octane; and 100 grams, boiling at 130°–160° C., which appeared to consist principally of nonane and decane. Only traces of hydrocarbons

of lower boiling point than octane were present. The addition of 5 per cent. of heptane to a sample of this oil lowered the flashing point to 97°. A specimen of "mineral sperm" oil which flashed above 212° F. was treated with different proportions by weight of pentane, hexane, and heptane, and the reduction of the flashing point noted.

Mixtures of Mineral Sperm Oil with Light Hydrocarbons.

Mineral sperm oil	95	per cent.,	pentane	5	per cent.,	flashes	110° F.
" "	" 90	" "	"	10	" "	"	ord. temp.
" "	" 95	" "	hexane	5	" "	"	110° F.
" "	" 90	" "	"	10	" "	"	ord. temp.
" "	" 95	" "	heptane	5	" "	"	145° F.
" "	" 90	" "	"	10	" "	"	110° F.
" "	" 83	" "	"	15	" "	"	96° F.
" "	" 80	" "	"	20	" "	"	ord. temp.

It is evident, therefore, that the low flashing point and danger of oils may be due not to the presence of small quantities of very volatile products, but rather to the large proportion which they contain of constituents of moderately high boiling point.

The burning test which determines the temperature at which a sample of oil may be set on fire and will burn in an open vessel, has been generally conceded to be unreliable as an indication of safety. Nevertheless, the laws of New York State prohibit the sale of oil which burns below 300° F. An oil may show a very high burning test and yet be of low flashing point and therefore extremely unsafe. This is especially the case with oils which consist of a mixture of very heavy and very light hydrocarbons. The more nearly homogeneous an oil is in composition the closer the flashing and burning points will approach each other. For example, the fractions corresponding to nonane and decane used in the experiments described above take fire at a temperature but little above their flashing points.

Nonane flashes 79° F., burns 110° F.
Decane " 104° " " 136° "

The flashing point of an oil is also, as is well known, dependent not only on the proportion of light constituents present, but upon the character of the oil as a whole. An unsafe oil may be brought up to legal standard by adding to it a sufficient quantity of heavy lubricating oil, but such a heterogeneous mixture will be of poor quality for burning purposes. It is doubtless this which has led manufacturers to make the oft-repeated claim that a high flashing

point is inconsistent with good burning qualities. If refiners would be content to make a little less oil, leaving out some of the benzine and some of the lubricating oil as well, there would be no difficulty in producing illuminating oils of high flashing point and excellent illuminating power. The well known Astral oil, which flashes at 125° F., is a standing protest against the claim of superior burning qualities for low-grade oils. This is simply the *heart* of the burning oil freed from both lighter and heavier deleterious ingredients. Tests made by the authors have shown that the above mentioned brand burns admirably in modern lamps, and by photometric tests gives results fully equal to any other oil in the market.

We are at present engaged in a series of experiments to determine the relative value as illuminating agents of the different hydrocarbons composing kerosene. The results of these experiments will form the material of another communication.

Only a very small amount of volatile material requires to be removed from an oil of ordinary character in order to raise its flashing point materially, as the following experiment shows.

One kilogram of an oil flashing at 108° F. was placed in a flask, and a gentle current of air at ordinary temperature aspirated through it during 24 hours. At the end of that time the oil was found to have lost 28 grams, or 2.8 per cent. in weight, and showed a flashing point of 116° F. Treatment of ordinary oils by a somewhat similar process would doubtless be effective in making them materially safer, and would probably add but a fraction of a cent per gallon to their cost.

It would be too much to expect of refiners that they should furnish oils of much higher flash test than they are required to do by law. The passage of a statute raising the legal standard to 120° would, however, cause no serious hardship to manufacturers, and would effect a saving of life and property which would far outweigh the very slightly increased cost of burning oil. It has been urged that with such a law manufacturers would simply add heavier products to their oils and thus bring them up to the legal standard, to the detriment of their burning qualities. This would, however, be in opposition to their own interest, since oils of high flash and excellent quality are already in the market and are extensively used.

The experiments described above show conclusively that an oil heated above its flashing point is dangerous, whether that point be

high or low. There can, therefore, be no doubt that in using kerosene of ordinary quality in the powerfully heating lamps which are now common, we are dependent for our safety upon the accurate construction of the burners, which render it difficult for the explosive vapors in the lamp to become ignited. An oil which flashes below 120° F. is not safe to use in these lamps, and with oils of ordinary grade the conditions of explosion are constantly present.